THERMAL STABILITY OF POLYOXOMETALATE COMPOUND OF KEGGIN K₆[β₂-SiW₁₁O₃₉]·nH₂O SUPPORTED WITH SiO₂

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ABSTRACT

Synthesis through sol-gel method and characterization of polyoxometalate compound of K₆[β₂-SiW₁₁O₃₉]·nH₂O supported with SiO₂ have been done. The functional groups of polyoxometalate compound was characterized by FT-IR spectrophotometer for the functional groups and the degree of crystallinity using XRD. The acidic of K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ was determined qualitative analysis using ammonia and pyridine adsorption and the quantitative analysis using potentiometric titration method. The results of FT-IR spectrum of K₆[β₂-SiW₁₁O₃₉]·nH₂O appeared at wavenumber 987.55 cm⁻¹ (W=O), 864.11 cm⁻¹ (W-Oe-W), 756.1 cm⁻¹ (W-Oe-W), 3425.58 cm⁻¹ (O-H), respectively and spectrum of K₆[β₂-SiW₁₁O₃₉]SiO₂ appeared at wavenumber 956.69 cm⁻¹ (W=O), 864.11 cm⁻¹ (W-Oe-W), 3448.7 cm⁻¹ (O-H), respectively. The diffraction of XRD pattern of K₆[β₂-SiW₁₁O₃₉]·nH₂O and K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ compounds show high crystallinity. The acidic properties showed K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ more acidic compared to K₆[β₂-SiW₁₁O₃₉]·nH₂O. The qualitative analysis showed pyridine compound adsorbed more of polyoxometalate compound of K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Analysis of stability showed that the K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ at temperature 500°C has structural changes compare to 200-400°C which was indicated from vibration at wavenumber 800-1000 cm⁻¹.

Keywords: K₆[β₂-SiW₁₁O₃₉]·nH₂O, polyoxometalate, SiO₂

INTRODUCTION

Polyoxometalate compound is the cluster compound of metal-oxygen which has acid-base properties, it has various structural and oxidation rates, so it is very effective for both acid-base reaction and reduction oxidation reaction catalyst (Yamase dkk, 2002). Polyoxometallic compounds are effective as catalysts because they have higher acidity than sulfuric acid and not toxic (Okuhara et al., 1996). This compound has been applied as a catalyst in industrial processes in developed countries such as Japan (Nakagawa and Mizuno, 2007).

The research of polyoxometalate compounds are primarily intended in terms of its superiority as a catalyst which can be performed either in homogeneous or heterogeneous systems depending on the medium are used. In a heterogeneous system, the polyoxometalate compound can be used repeatedly in catalytic reaction.

The polyoxometalate compound has a low surface area and high solubility in a polar solvent (Kim et al., 2006). The Catalyst which have a small surface area is suitable for homogeneous catalysts while the homogeneous catalysts can not be recycled. To designed the polyoxometalate compound as a heterogeneous catalyst, modification should carried out by embedding. Modification of polyoxometalate compounds can be embedding by inclusion using both metal oxide and non-oxide metals (Nerwman et al., 2006). The embedding is carried out to have a large surface area which can be used as heterogeneous catalysis and can increase the acidity of the compound, so that the catalytic properties increase. The catalytic activity is affected by the temperature, surface area, and acidity of the catalyst. The temperature affects collisions between molecules and certain chemical reactions require heating at high temperatures to obtain maximum results. As an example the hydroxylation reaction of n-hexane requires the temperatures above 400 °C and requires the Bronsted acid side in the reaction to obtain a high percent conversion (Eid et al., 2013).

The synthesis of H₃[γ-H₂SiV₂W₆O₂₆] has been carried out with various variations of embedding SiO₂, TiO₂, ZrOCl₂ and TaCl₅ by Karim (2014), which the product material has not been tested for its qualitative and quantitative acidity. Meanwhile Marci et al. (2013) has carried out the research by embedding Keggin H₃PW₁₂O₄₀ type polyoxometalate compounds with various metal oxides such TiO₂, SiO₂, ZrO₂, ZnO, and Al₂O₃. From the many several metal oxides which has been used, polyoxometalate compounds which are embedded with SiO₂ have higher catalytic character which applied to the propene hydration reaction.

In this research, the synthesis of Keggin K₆[β₂-SiW₁₁O₃₉]·nH₂O polyoxometalate compound which is embedded by SiO₂ metal oxide. The metal oxide of SiO₂ was obtained from reaction of tetraethyl orthosilicate (TEOS) as the sol gel method. The embedded result of synthesized polyoxometalate compounds were characterized by a Fourier Transform Infrared (FT-IR) spectrophotometer and X-Ray Diffractometer (XRD). Polyoxometalate compounds K₆[β₂-SiW₁₁O₃₉]·nH₂O was soaked on the acid compounds before and after embedded qualitatively and quantitatively. The thermal stability character of K₆[β₂-SiW₁₁O₃₉]·nH₂O and K₆[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ were tested by heating it at various temperature using furnace and the heating results were
characterized by a FT-IR spectrophotometer. The acidity and thermal stability character of polyoxometalate compounds were tested prior to be used as catalysts in chemical reactions that require heating at high temperatures.

EXPERIMENTAL SECTION

The instruments which used in this research X-Ray diffractometer (XRD) Rigaku MiniFlex 600 and FT-IR Shimadzu Prestige-21 Spectrophotometer. The substances used in this research were sodium metasilicate (Na₂SiO₃), sodium tungstate (Na₂WO₄), hydrochloric acid (HCl), potassium chloride (KCl), potassium carbonate (K₂CO₃), tetraethyl orthosilicate (TEOS), Sodium bis (2-Ethylhexyl) sulfosuccinate, cyclohexane, pyridine, ammonia (NH₃), n-butyamine, acetonitrile and aquades (H₂O).

Synthesis of Polyoxometalate Compounds K₃[β₂-SiW₁₀O₃₉]∙nH₂O and Its Characterization

The acidity test of compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O was performed with addition of potassium chloride (KCl) to the compound [β₂-SiW₁₀O₃₉]∙nH₂O acting as a K⁺ ion donor. At the end of the synthesis process there was obtained a white solid which was a compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O. The synthesis of compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O and K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ was characterized by a FT-IR spectrophotometer and X-Ray diffractometer (XRD).

The synthesis K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ with Sol-gel Method and Its Characterization

The synthesis of composite K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ was modified from the procedure of Kim et al. (2006), Sodium bis (2-ethylhexyl) sulfosuccinate of 1.5 g was dissolved with 1 mL of cyclohexane (solvent A). The compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O∙0.76 g was dissolved with slightly aquades (solvent B). Solvent B was added to solvent A while stirring. A total of 11.2 mL of tetraethyl orthosilicate (TEOS) was added dropwise. Stirred with stirrer and heated at 60°C for 2 hours. The white solids formed are K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ and dried by vacuum. The compounds K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ are characterized by a FT-IR spectrophotometer, and X-Ray diffractometer (XRD).

The acidity test of compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O and K₃[γ-SiW₁₀O₃₉]∙nH₂O/SiO₂ is qualitatively

A total of 0.5 g of each K₃[β₂-SiW₁₀O₃₉]∙nH₂O and K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ were inserted into vials. A total of 10 mL of pyridine and 25% ammonia (NH₃) were each fed into a beaker glass. A vial bottle was inserted into a beaker glass containing pyridine and ammonia and then sealed tightly with a kreb plastic. The compound was allowed for two days to adsorption between pyridine and ammonia with polyoxometalate compounds. Compounds that have been in contact with pyridine and ammonia were tested qualitatively by characterizing using a FT-IR spectrophotometer.

The thermal stability test K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂

The thermal stability test K₃[β₂-SiW₁₀O₃₉]∙nH₂O/SiO₂ was heated at 200 °C, 300 °C, 400 °C and 500 °C for 2 hours in the furnace. The heating compound was cooled and characterized by an FTIR spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Keggin type Polyoxometalate Compounds K₃[β₂-SiW₁₀O₃₉]∙nH₂O

The synthesis of compound K₃[β₂-SiW₁₀O₃₉]∙nH₂O was performed by addition of potassium chloride (KCl) to the compound [β₂-SiW₁₀O₃₉]∙nH₂O acting as a K⁺ ion donor. The result of synthesis in the form of white solid was then characterized using FT-IR spectrophotometer which aims to identify the functional group formed as shown in Figure 1.

The peaks of the functional groups of polyoxometalate compounds appearing at wave numbers 4000-300 cm⁻¹ shows in Figure 1. The principal uptake of K₃[β₂-SiW₁₀O₃₉]∙nH₂O compounds shows the presence of vibration W = O appears in the 987.55 cm⁻¹ region, the W-O-W vibration of 864.11 cm⁻¹ in which oxygen is located on the edge of the compound Polyoxometalate and wave number 756.1 cm⁻¹ for the vibration of the W-O-W group which is the oxygen atom located at the center of the polyoxometalate compound. According to Okuhara (et al 2001), the absorption of polyoxometalate compounds has W=O groups at wave number 980 cm⁻¹,
vibration of W-O-W group 878 cm\(^{-1}\) and of vibration of W-O-W 779 cm\(^{-1}\). The compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ synthesis results in this study is in accordance with vibrations according to Okuhara (et al 2001). In addition to the 3425.58 cm\(^{-1}\) wave numbers indicating the vibration -OH which indicates the presence of H_2O in the polyoxometalate compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$. The presence of a hydrogen bonding effect is characterized by a widened peak in the FT-IR spectrum of Stuart (2004). $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$.

After the compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ was characterized using FT-IR spectrophotometer, then the polyoxometalate compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ was analyzed by XRD. Diffractogram of $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ polyoxometalate compound \( \cdot nH_2O \) is presented in Figure 2.

**Figure 2. XRD Diffraction Patterns Polyoxometalate Compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$**

Figure 2 shows the diffraction for the polyoxometalate compounds $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ with the highest intensity arising at 8°, 9°, 17°, 24° and 35° diffraction angles. According to Yang (et al 2011) the diffraction for polyoxometalates compounds is present in some diffraction regions, ie 6-10°, 15-20°, 22-25°, and 35-40°. The diffraction that appears below 10° in region 29 shows that the polyoxometalate compound has a very high crystallinity. Diffractogram of $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ compounds exhibiting sharp diffraction peaks indicates polyoxometalate $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ has very high crystalline properties in which the atoms of the polyoxometalate compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ is arranged regularly based on the length and angle of regular bonding.

**Synthesis of Keggin Type Polyoxometalate Compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ and Characterization**

The polyoxometalate compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ which has been obtained was further prepared by proportion to SiO\(_2\) obtained from TEOS hydrolysis. The embodiment was carried out by using a microemulsion and sol-gel method. Eriksson (et al 2004) describes that microemulsions are liquids derived from a mixture of water, hydrocarbons, and surfactants. Polyoxometalate compounds $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ synthesis and characterization by functional group analysis using FT-IR spectrophotometer with FT-IR spectra presented in Figure 3. The result of identification using FT-IR spectrophotometer to compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ shows the specific vibration of polyoxometal and SiO\(_2\) compounds.

Figure 3 shows the difference shown by the FT-IR spectrum of the polyoxometalate compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ before being carried out with SiO\(_2\). According to Derrick (et al 1999) the symmetric vibration of Si-O-Si is at the wave number 1130-1000 cm\(^{-1}\). Smith (1999) reported that the vibration of Si-O-Si symmetric stretching was stronger at 1085 cm\(^{-1}\). The FTIR spectra of compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ undergo a shift of wave numbers for asymmetric Si-O-Si stretch vibration at 1103.28 cm\(^{-1}\). The shift of wave numbers occurs in vibration W=O. The W=O vibe before it is presented appears at the wave number 987.55 cm\(^{-1}\) and the vibration after carrying with SiO\(_2\) appears at the wave number 956.69 cm\(^{-1}\). According to Stuart (2004) vibration -OH vibration in the presence of hydrogen bonding effect is in the range of 3500-2500 cm\(^{-1}\) wavelength characterized by a widened peak on the FT-IR spectra. Figure 3 (B) experiences a shift in the number of waves at the peak of 3448.72 cm\(^{-1}\) identifies the -OH vibration by the presence of H_2O on the $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ and the wave number at peak 3425.38 cm\(^{-1}\) identifies vibration -OH by the presence of H_2O in the compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$. The primary wave numbers of $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ and $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$ are presented in Table 1.

<table>
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<th>Vibration Number</th>
<th>Vibration Number</th>
<th>Vibration Number</th>
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<tr>
<td>$K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$</td>
<td>$K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$</td>
<td>$K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$</td>
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<tr>
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<td>756.1</td>
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<td>-</td>
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</tr>
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The polyoxometalate compound \( \cdot K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O \) which was supported with SiO\(_2\) then characterized using XRD. The diffraction angle and crystallinity of polyoxometalate compounds $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O/SiO_2$. Comparison of XRD of compound $K[\beta_2-SiW_{11}O_{39}]\cdot nH_2O$ with $K[\beta_2$-
SiW₁₁O₃₉]∙nH₂O/SiO₂ are presented in Figure 4. (A) K₄[β₂-SiW₁₁O₃₉]∙nH₂O diffraction emerging below 10° in region 2θ indicates that the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O has very high crystalline properties due to the atom of the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O is arranged regularly based on the length and angle of bond formed. Figure 4 (B) shows the XRD pattern of K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂. The compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ has a high crystallinity with a diffraction angle of 2θ each at 8°, 18°, 27°, and 34° indicating the characteristics of the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ in which the atoms of the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ were arranged regularly on the basis and length of the regular bonding. Figure 4 (B) shows the pattern of XRD K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ indicating a change in the diffraction angle.

Figure 4. The diffraction pattern of K₄[β₂-SiW₁₁O₃₉]∙nH₂O (A), diffraction pattern of K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ (B)

The acidity test of compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O and K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ in qualitatively

**The Acidity test of K₄[β₂-SiW₁₁O₃₉]∙nH₂O**

The acidity measurement of the polyoxometalate compound · K₄[β₂-SiW₁₁O₃₉]∙nH₂O is carried out both qualitatively and quantitatively. The FT-IR spectrophotometer method was performed for qualitatively, where K₄[β₂-SiW₁₁O₃₉]∙nH₂O polyoxometalate compound was saturated with ammonia and with pyridine for 2 days resulting in adsorption on the surface of K₄[β₂-SiW₁₁O₃₉]∙nH₂O. The saturation result were compared before or after being saturated with ammonia or pyridine. The saturation result was measured by a FTIR spectrophotometer. The FTIR spectra K₄[β₂-SiW₁₁O₃₉]∙nH₂O saturation result shown in Figure 5.

Polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O of the FT-IR spectra of Figure 5 shows no absorption bands at 1400-1440 cm⁻¹ wavelengths on a K₄[β₂-SiW₁₁O₃₉]∙nH₂O saturated polyoxometalate compound with or without saturation Pyridine. According to Dines (et al., 1991) ammonia forms ammonium ions (NH₄⁺) with the observed wave numbers at 1400-1440 cm⁻¹, but in the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O not exhibit ammonium ion vibrations (NH₄⁺) at wave number 1400-1440 cm⁻¹. Ammonia can be adsorbed on the acid side of the heteropoly compound and in the metal cation (Seo et al., 1988). Ammonia was not adsorbed on the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O. It was possible that the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O does not exhibit ammonium ion vibration (NH₄⁺) at wave numbers 1400-1440 cm⁻¹. Figure 5 (B) shows a vibration of -OH at a wave number of 3448.72 cm⁻¹ which identifies the presence of H₂O in a polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O. According to Stuart (2004), vibration -OH vibration, with the effect of hydrogen bonds in the range of 3500-2500 cm⁻¹ wavelengths characterized by wider peaks in the FT-IR spectra.

Figure 5. FTIR spectrum of polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O (A), FTIR spectra of polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O. Saturation with ammonia (B), FT-IR spectra of polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O saturation with pyridine (C)

Polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O compounds with saturation with pyridine in Figure 5 (C) exhibit an -OH shift vibration appearing at a 3425.58 cm⁻¹ wave number identifying H₂O in a polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O. According to Khalifah and Prasetyo (2008) pyridine molecules bound to Lewis acid sites absorbed at wave numbers 1400-1700 cm⁻¹. Figure 5 (C) FT-IR spectra does not show the wave number. In this case, pyridine was unsorbed in the polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O. FT-IR digital specimen data of K₄[β₂-SiW₁₁O₃₉]∙nH₂O compounds with saturation with ammonia and pyridine.

**The Acidity Test of K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂**

The compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ was saturated using ammonia and pyridine. Then the material was characterized by an FT-IR spectrophotometer. The saturation result was measured by an FTIR. The FT-IR spectra of K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ of the saturation results are shown in Figure 6.

Figure 6 (A) shows the FTIR spectra of a polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ before being saturated. Figure 6 (B) shows the FTIR spectra of a polyoxometalate compound K₄[β₂-SiW₁₁O₃₉]∙nH₂O/SiO₂ with saturation using
ammonia. Dennis et al (1991) states that ammonia forms an ammonium ion (NH₄⁺) with an observed wave number at 1400-1440 cm⁻¹. Seo et al (1988) states that ammonia can be adsorbed on the acid side of the heteropoly compound and in the metal cation. The compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ exhibits the vibration of the NH₄⁺ ammonium ion appearing at the wave number 1404.18 cm⁻¹.

Figure 6. FTIR spectra of polyoxometalate compounds K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ (A), FT-IR spectra of polyoxometalate compounds K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Saturation with ammonia (B), FT-IR spectra of polyhydroxide compound K₈[β₂-K₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturation with pyridine (C).

Polyoxometalate compounds K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturated with ammonia absorbance bands not found at wavelength 1400-1440 cm⁻¹. In this case it is possible that the ammonia was not adsorbed on the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. Stuart (2004) states that vibration -OH vibration in the presence of hydrogen bonding effect is in the range of 3500-2500 cm⁻¹ wavelengths characterized by a widened peak on the FTIR spectra. Polyoxometalate compounds K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ exhibit a -OH loop vibration at 3425.58 cm⁻¹ wave numbers identifying the presence of H₂O in the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂.

Figure 6 (C) shows the spectra of K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ compounds with saturation using ammonia also exhibiting a -OH looping vibration at 3425.58 cm⁻¹ wave number that identifies the presence of H₂O in the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. The Caliph and Prasetyoko (2008) explain that pyridine molecules bound to Lewis acid sites are absorbed at wave numbers 1400-1700 cm⁻¹. Picture no. 10 (C) shows that the pyridine molecule has been adsorbed by the polyoxometalate compound K₈[β₂-K₂-SiW₁₁O₃₉]·nH₂O/SiO₂ shown in the wave number 1481.33 cm⁻¹. This shows that the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ has Lewis acid character.

Based on the FTIR spectrum of Figure 5 and 6, it can be seen that the wave number 1404.18 cm⁻¹ is a vibration of the ammonium ion NH₄⁺. The compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ saturated with ammonia (Figure 6 B) does not show the uptake of ammonia molecules at the 1404.18 cm⁻¹ wave number as well as the compound K₈[β₂-SiW₁₁O₃₉]·nH₂O (Figure 5 B). In this case the ammonia is not adsorbed on the compound K₂[β₂-SiW₁₁O₃₉]·nH₂O and the compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. The FT-IR spectra at Figure 5 (C) does not show the uptake of pyridine molecules at the 1404.18 cm⁻¹ wave number while the FT-IR spectra of Figure 6 (C) of K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ see the wave number 1481.33 cm⁻¹ but does not show sharp spectra. It can be concluded that qualitatively pyridine adsorbed more on the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂.

The acidity test of compound K₂[β₂-SiW₁₁O₃₉]·nH₂O and K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ in Quantitative

The acidity measurements of the K₂[β₂-SiW₁₁O₃₉]·nH₂O and K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ compounds were quantitatively measured by titration of potentiometric potassium using n-butylamine as titrant and acetonitrile as solvent. Acetonitrile is an aprotic solvent as a solvent on the compound K₂[β₂-SiW₁₁O₃₉]·nH₂O and K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ so that only the acidity of K₂[β₂-SiW₁₁O₃₉]·nH₂O and K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂. According to Pecchi et al (1985) using benzene solvent, acetonitrile and iso-octane as solvents in potentiometric titration and selected acetonitrile as a polar solvent to avoid the adsorption of n-butylamine and acetonitrile as an inert solvent.

The measurement by potentiometric method can determine the total acidity and acidity strengths of a polyoxometalate compound. The initial potential value (E₁) identifies acidity strength from the surface side and classifies the acidity strength based on the range that classifies in scale: : E₁ > 100 mV (acidity is very strong), 0 < E₁ < 100 mV (strong acidity), -100 < E₁ < 0 mV (weak acidity), E₁ < -100 mV (acidity is very weak) (Romanelli et al, 2004). The first derivative curve and the second derivative are made to be able to see where the titration equivalence point is shown in Figure 11. The equivalent point was performed to see the condition in which the base of n-butylamine is added precisely reacts with the acidic K₂[β₂-SiW₁₁O₃₉]·nH₂O nH₂O which was titrated. In addition, an equivalence point is performed to determine the amount of base volume of n-butylamine required to neutralize K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ acid.

Figure 7 shows the results of measurement of the compound K₂[β₂-SiW₁₁O₃₉]·nH₂O has an initial potential value of 54.4 mV. Based on the potential value range of 0 < E₁ < 100 the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O has a strong acid side. The titration equivalence point is at 0.2 mL of n-butylamine volume reinforced by the first derivative curve and the second derivative of potentiometric titration. The titration equivalence point can be observed with sharp potential changes (Mulja and Suharman, 1995). Figure 8 and 9 show the first derivative curves and the second derivative curves of the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O.

The measurement of the acidity level of the polyoxometalate compound K₂[β₂-SiW₁₁O₃₉]·nH₂O/SiO₂ is also carried out through potentiometric titration. From the titration curve presented in Figure 10, the titration equivalent point was obtained at the time of titration volume 0.4 mL n-butylamin. Based on the data of the equivalence point it is found that the
polyoxometalate $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ compound requires more base volume of n-butylamine to neutralize the polyoxometalate compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$. This indicates that $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ is more acidic than a polyoxometalate compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O$. This is also supported by looking at the potential initial value comparison. The initial potential value of $K_{d}[β_2SiW_{11}O_{39}]nH_2O/$SiO$_2$ is 76.6 mV whereas the initial potential value of $K_{d}[β_2SiW_{11}O_{39}]nH_2O$ is 54.4 mV. The compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ is included in the acidic acid classification strong based on the potential value range of acid strength. Increased density of polyoxometalate compounds $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ because the compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O$ interacts with the carrier SiO$_2$.

Figure 7. Potentiometric titration curve of compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O$

Figure 8. The first derivative titration curve of potentiometric titration of compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O$

Figure 9. The second derivative titration curve of potentiometric titration of compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O$

Figure 10. Potentiometric titration curve of compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$

Figure 11. The first derivative titration curve, potentiometric titration of compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$

Potentiometric titration method is an analytical technique based on the potential measurement of a sensor or electrode. The electrodes used are glass-containing glassed electrode, the liquid having the potential difference properties between the membrane and the electrolyte in contact with the membrane is determined by the activity of the particular ion. The membrane electrode used is a glass electrode. These glass electrodes are said to be ion-selective because they are specific only to $H^+$ ions. Potential measurements of polyoxometalate compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ can be performed with potentiometric titration because the compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ has $H^+$ ions. Potentiometric titration curve of $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ can be seen in Figure 10.

The thermal Stability Compound of $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$

The compound $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$ of results the preparation was heated at various temperatures to see the thermal stability of $K_{d}[β_2SiW_{11}O_{39}]nH_2O/SiO_2$. The heating results at various temperatures were characterized by FTIR.
spectrophotometers. Figure 13 shows the FT-IR spectra of the wavelengths that appear on the K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O and K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ unheated and heated at various temperatures from 200-500°C.

Figure 13 shows the difference shown by the FT-IR spectra of the K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O compound before being carried out with SiO$_2$ or after heating. Based on the FTIR spectrum the warming of vibrations emerging undergoes a shift in the number of waves. Figure 13 (A) and (B) show the wave numbers 3425.58 cm$^{-1}$ and 3448.72 cm$^{-1}$ while in Figure 13 (C), (D), (E) and (F) indicate wave numbers 3433.29 cm$^{-1}$, 3441.01 cm$^{-1}$, 3425.58 cm$^{-1}$, 3402.43 cm$^{-1}$ identified as -OH groups in the presence of H$_2$O with a slight amount seen from percent transmittance. Figure 13 (F) shows excellent thermal stability properties in the presence of small amount of H$_2$O which was characterized by a shift in the wavelength number of the -OH group. The vibration of polyoxometalate compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ in the 800-1000 cm$^{-1}$ wave range at 500°C shows slight differences due to vibration W=O overlapping with vibrations W-O-W and W-O-W. This suggests that on increasing the heating temperature may cause changes in the structure of polyoxometalate compounds. Table 2 shows the vibrations of the K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O , K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ without heating and after heating at a temperature of 200°C - 500°C.

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CONCLUSION

Polyoxometalate compounds K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O and K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ were synthesized. The main vibration of the IR spectra of K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O shows the presence of vibration W=O appears in the area of 987.55 cm$^{-1}$, W=O-W appears in the area of 859.61 cm$^{-1}$, W-O-W appears in the area of 756.1 cm$^{-1}$, O=H is O=H appears in the area of 3425.58 cm$^{-1}$ and for the compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ vibration W=O appears in the region 956.69 cm$^{-1}$, W=O-W appears at 864.11 cm$^{-1}$ and -OH area appears at 3448.72 cm$^{-1}$. The XRD diffraction pattern for K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O differs at the diffraction angles of 8°, 9°, 17°, 24°, 35° and for the compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ appears at the angle of diffraction of 2θ each of 8°, 18°, 27° and 34°. Polyoxometalate compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ with a potential value of 76.6 mV has a higher acidity value than the compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O having a potential value of 54.3 mV. Qualitative analysis by using ammonia and pyridine to compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O and K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ it was found that the pyridine compound adsorbed more on the polyoxometalate compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$. The thermal stability test of the compound K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ shows at a temperature of 500°C of K$_2$[β$_2$SiW$_{11}$O$_{39}$]·nH$_2$O/SiO$_2$ compound slightly altered the structure of the polyoxometalate compound characterized by overlapping of vibrations in the range of 800-1000 cm$^{-1}$.

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